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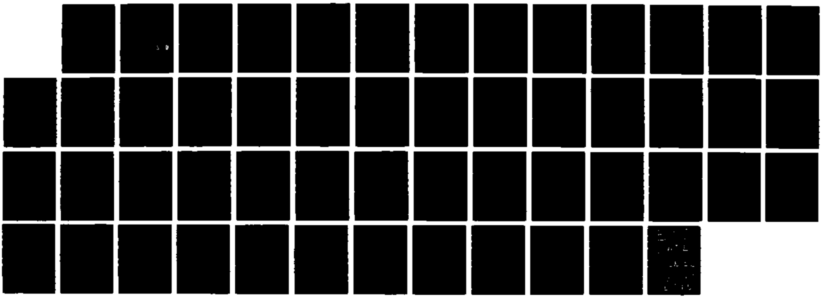

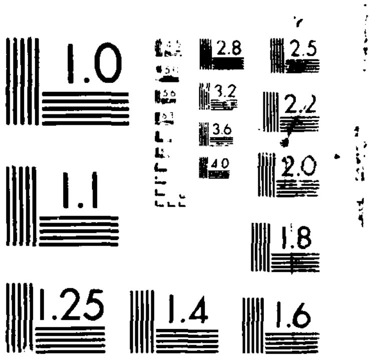
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THE IMPACT OF HOUSEHOLD HAZARDOUS WASTES

ON LANDFILL LEACHATES

by

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Most importantly, I would like to dedicate this thesis to my wife, Terri, and my son, Paul, and thank them for their love, patience, and encouragement during our stay at RPI and always.

ABSTRACT

Protective measures have been enacted to mitigate the deleterious effects of landfill leachate on ground and surface waters. One such measure has been to remove items classified as Household Hazardous Wastes from the solid waste stream prior to landfill disposal. Even though the alternative methods of disposal may be very costly, no effort has been made to assess the impact of Household Hazardous Wastes on landfill leachates and, subsequently, on receiving waters. Therefore, a model is needed to assess this impact accurately and determine which, indeed if any, items should be removed from the solid waste stream prior to landfill disposal.

The model proposed to assess the impact of Household Hazardous Wastes is developed in two steps. First, the model considers only the effects of dilution of the landfill leachate on the concentration of a particular contaminant. Next, the attenuation of contaminants within the landfill mass is treated by the addition of an attenuation factor. However, the "shape" and magnitude of this factor is unknown.

The proposed model is used to perform a sample calculation to determine the amount of a specific contaminant, Diazinon, that must be disposed of in a landfill with specified operational parameters in order to exceeded the New York State drinking water standard. This

calculation amplifies the research necessary to assess the impact of Household Hazardous Wastes. This research includes a more complete characterization of the Household Hazardous Waste stream. Also, a better understanding of the attenuation of contaminants within the landfill is needed. Leachate production must be accurately predicted in order to apply the dilution model. Finally, the accuracy of the estimation of the dilution of contaminants by the use of the EPTOX test-based model must be determined.

CHAPTER I

INTRODUCTION

The contamination of groundwater by landfill leachate is well documented (e.g., Kelly, 1976, DeWalle and Chian, 1979, Brower and Ramkrishnadas, 1982). Landfill leachate composition varies widely, consisting of organics resulting from the anaerobic degradation of the refuse, organic chemicals including pesticides, herbicides, and solvents, and inorganics, especially significant heavy metal concentrations. Table 1 details leachate analyses of some landfills in Norway and the Pacific Northwest of the United States (Johansen and Carlson, 1976), while Table 2 illustrates the range of values for leachate constituents based on a survey of 18 different sanitary landfills in the United States (Chian and DeWalle, 1976). As these tables illustrate, organics usually are not identified by species, rather they are collectively described in terms of oxygen demand. Table 3 is an excerpt of the analysis of leachate organics (Khare and Dondero, 1977) from a small-town municipal sanitary landfill in upstate New York. Overall, 40 organic compounds were identified.

The presence of organic solvents, pesticides, and heavy metals in landfill leachate has provided impetus for efforts to eliminate some of the sources of these contaminants. Since sanitary landfills generally service residential customers, efforts to stop the pollution from

Table 1

Sample Leachate Analysis

Constituent	Gronmo Norway	Isi Norway	Cedar Hills, USA	Kent Highland, USA
COD (mg/l)	470	110	38800	3800
BOD (mg/l)	320	50	24500	2460
pH	6.8	6.4	5.4	6.4
Mg (mg Mg/l)	66	13	-	-
Cl (mg Cl/l)	680	68	-	-
Fe (mg Fe/l)	67.6	11.5	810	245
Zn (mg Zn/l)	0.055	0.12	155	5.30
Cr (mg Cr/l)	0.023	0.002	1.05	0.05
Ni (mg Ni/l)	< 0.1	0.005	1.20	0.10
Cu (mg Cu/l)	0.085	0.008	1.30	0.18
Cd (mg Cd/l)	0.0005	0.0005	0.03	0.01
Pb (mg Pb/l)	0.004	0.001	1.4	< 0.1
Co (mg Co/l)	-	0.033	-	

(Johansen and Carlson, 1976)

Table 2

Range of Leachate Constituents

Constituent		Range of Values
COD	mg/l	40 - 89520
BOD	mg/l	81 - 33360
pH		3.7 - 8.5
Mg	mg Mg/l	17 - 15600
Cl	mg Cl/l	4.7 - 2467
Mn	mg Mn/l	0.09 -125
Fe	mg Fe/l	0.6 - 2820
Zn	mg Zn/l	0.05 - 370
Cu	mg Cu/l	< 0.2 - 9.9
Cd	mg Cd/l	0.03 - 17
Pb	mg Pb/l	< 0.10 - 2.0

(Chian and DeWalle, 1976)

Table 3

Leachate Organic Analysis

Compound
Ethane
Ethylene
1-Pentene
Hexane
Heptane
Nonane
Decane
Chloroform
Carbon tetrachloride
Benzene
Toluene
Xylene
2-hexanol
Methanol
Ethanol
4-Methyl-2-pentanol
Methylamine hydrochloride
2-Methyethylenimine
Di-n-butylamine
Propanamide
Acetone
2-Butanone
Acetic Acid
Propionic Acid
Butyric Acid

(Khare and Dondero, 1977)

this particular source have spawned the term Household Hazardous Waste. Household Hazardous Waste may be defined (EPA, 1986) as a waste originating from homes and consisting, in whole or in part, of a compound listed in 40 CFR 261.33 (e) or (f). Also, a waste is a Household Hazardous Waste if it is ignitable, corrosive, reactive, or toxic, as defined in 40 CFR 261.21 -261.24. There is a plethora of Household Hazardous Wastes and associated hazardous components. Table 4 is a small sample of the diversity of Household Hazardous Wastes (EPA, 1986).

The source of a contaminant in landfill leachate may or may not be easily identified depending on the particular contaminant. Some contaminants may be ubiquitous and, thus, it will be virtually impossible to stop their flow into a landfill. Examples are lead and cadmium, which are used in paints and dyes. In order to stop their flow into a landfill it would almost be necessary to find alternate means of disposal for all painted items and vinyl upholstery. Other contaminants, such as pesticides and certain solvents are easily identified and, therefore, more readily removed from the solid waste stream (if necessary).

The purpose of this work is to determine the research necessary to assess the impact of Household Hazardous Wastes. The ultimate goal is to determine which Household Hazardous Waste components must be removed from the solid waste stream prior to landfill disposal, and which ones are

Table 4

Sample Household Hazardous Wastes

General Class	Subclass	Component
Household Cleaners	Wood/Metal Cleaners/Polishers	Petroleum Distillates Petroleum Naptha Turpentine Isopropyl Alcohol
Automotive Products	Oil/Fuel Additives	Xylene Methanol Ethyl Ether sec-Butanol
	Carburetor/FI Cleaners	Toluene Butanone Acetone Methyl Chloride
Home Maintenance Products	Paint Thinners	Isopropylacetone
	Adhesives	Butyl Acetate Tetrahydrofuran Acrylic Acid Cyclohexane Formaldehyde
Lawn/Garden Products	Herbicides	2,4-D Silvex
	Pesticides	Aldrin Chlordane DDT Trichlorophenol Parathion

(EPA, 1986)

sufficiently attenuated to make their removal unnecessary. A literature review is conducted for several reasons. Efforts to characterize Household Hazardous Wastes are discussed to determine the magnitude of this fraction of the solid waste stream and its particular components. Two methods for determining leachate production are reviewed since the movement of contaminants in a landfill is dependent upon the content and spatial and temporal distribution of moisture within a landfill site. The interactions of metal ions are summarized in an effort to understand how heavy metals may be attenuated in the landfill. The mechanisms of biodegradation and adsorption are discussed as they may also be factors in the attenuation of contaminants in the leachate. Next, the EP Toxicity (EPTOX) Test is reviewed as it is used as a basis for the determination of the dilution of contaminants by ground water. Finally, a dilution model is developed and a sample calculation is performed to amplify the need to conduct additional research so that the impact of Household Hazardous Wastes can be assessed accurately.

CHAPTER II

LITERATURE REVIEW

A. Quantifying Household Hazardous Waste

Efforts to quantify and characterize Household Hazardous Wastes in the solid waste stream typically follow one of three strategies. The first strategy consists simply of conducting a survey. Unfortunately, this method's accuracy is largely dependent on the recollections of the respondents. The second approach is to sort the municipal refuse after it has been collected, identifying the hazardous components. Finally, Household Hazardous Wastes may be characterized and quantified by inventorying the wastes brought into Household Hazardous Waste collection projects.

The Household Hazardous Waste Disposal Project in Seattle, WA (Galvin and Guss, 1982), surveyed households to determine if they had any of the ten substances listed in Table 5 in their homes. Although the percentages are, in some cases, quite high, two-thirds of the respondents had not disposed of any of these same items in the year prior to being questioned. This study gives a characterization of the Household Hazardous Waste stream, however, there are no estimates of the quantities generated.

Similarly, a survey conducted in Massachusetts (Laderman et al, 1985) questioned households to determine if they had disposed of anything on a list of ten items,

Table 5
Seattle Households with Hazardous Wastes

Substance	Total (%)
Household Cleaners	98
Auto/Furniture Polishes	80
Paints/Thinners	78
Motor Oil	59
Pesticides	56
Fertilizers	56
Drain Opener	55
Weed Killer	49
Antifreeze	41
Wood Preservatives	34

(Galvin and Guss, 1982)

how much was discarded, and the method of disposal. The results of this survey are presented in Table 6. The method of disposal (ground, sewer, landfill) is not further distinguished, thus the effect on landfill leachate is uncertain. The annual disposal quantity for the state is from an extrapolation based on population and, therefore, assumes a representative sample was taken.

Sorting municipal solid waste after collection has the advantage of directly sampling what will go into the landfill. A study of the Seattle/King County area (Cal Recovery Systems, 1985) determined that approximately 0.5 percent (by weight) of the municipal solid waste stream are Household Hazardous Wastes. This represents half of the 11,000 tons per year of hazardous wastes that are disposed of in that area's landfills.

Perhaps the most well documented study of the character of Household Hazardous Wastes was conducted in Marin County, California, and New Orleans, Louisiana (Rathje et al, 1987). 11.4 metric tons of household refuse from 1,061 collections (households) were sorted in New Orleans. In Marin County, 15.4 metric tons from 1,022 collections were sorted. It is estimated that, at least, 0.35 to 0.40 percent of the solid waste collected is hazardous. These quantities extrapolate to approximately 642 metric tons of Household Hazardous Wastes per year for the New Orleans study area and approximately 259 metric

Table 6

Disposal of Household Hazardous Wastes in Massachusetts

Substance	Avg. per Household	Annually Disposed Statewide	% in Ground, Sewer, Landfill
Oil	14 qts	8,700,000 qts	57
Paint	2.4 qts	480,000 qts	91
Pesticides	2 cans	360,000 cans	98
Antifreeze	20 qts	3,000,000 qts	95
Batteries	1	120,000	68
Asphalt	4 qts	170,000	100
Gas/Kerosene	4 qts	180,000 qts	64
Radiator Flush	1 can	32,000 cans	86
Herbicides	2 cans	44,000 cans	80
Chemicals	-	-	75

(Laderman et al, 1985)

tons for Marin County. The percentages of waste type by item class and by weight are detailed in Tables 7 and 8. Batteries and electrical items were discarded with the greatest frequency in both New Orleans and Marin County, while household maintenance items made up the largest fraction by weight in both areas. Although each area differs on a socio-demographic scale, Tables 7 and 8 illustrate that the Household Hazardous Waste stream from each is similar.

There are several limitations to this study. Refuse was collected from single family dwellings only and, therefore, may not accurately represent the household hazardous waste generated by apartments and other multi-unit dwellings. Also, a hazardous product was only weighed if an appreciable amount was present. Mostly-empty containers and packages were not weighed nor were paint brushes, oily rags, and other contaminated items. Finally, due to the short sampling and overall project durations, seasonal variations are not accounted for.

A project conducted by the Stanford Research Institute is now underway to determine the concentration of household hazardous waste in municipal solid waste (Galvin, 1987). A set of generic recipes has been formulated by product class to aid in extrapolating the sample concentrations to the overall concentration. Initial results estimate that 0.35 percent of municipal solid waste is composed of Household

Table 7

Comparison of Household Hazardous Wastes between New Orleans, LA and Marin County, CA by Item Type

Waste Type	% of Total Number of Household Hazardous Waste Items	
	New Orleans	Marin County
Household Cleaners	10.9	10.2
Auto Maintenance	3.3	3.2
Household Maintenance	10.7	9.9
Pesticides/Lawn Care	1.6	3.8
Batteries/Electrical	29.9	48.8
Prescription Drugs	10.2	4.4
Selected Cosmetics	29.7	17.2
Other	3.6	2.7

(Rathje et al, 1987)

Table 8

Comparison of Household Hazardous Wastes between New Orleans, LA and Marin County, CA by Weight

Waste Type	% Weight of Total Household Hazardous Waste	
	New Orleans	Marin County
Household Cleaners	13.2	15.0
Auto Maintenance	21.2	11.6
Household Maintenance	43.3	27.8
Pesticides/Lawn Care	1.0	8.8
Batteries/Electrical	11.9	26.6
Prescription Drugs	1.1	3.2
Selected Cosmetics	5.0	3.8
Other	3.4	3.2

(Rathje et al, 1987)

Hazardous Waste constituents. No information is available, as of yet, on the computational procedures used in this study.

A report from the Minnesota Pollution Control Agency contains the results of inventories of the wastes brought voluntarily to Household Hazardous Waste collection points in that state (Ridgley, 1987). The communities in which these points were established consistently had participation rates of about 2.3 percent. The most frequently collected item was oil paint as indicated in Table 9 which summarizes the weight fractions of all the wastes collected. Again, as in the Marin County/New Orleans study, oil was the largest by-weight substance. It is difficult to put the ounces per participant in terms of annual generation as these collection points were established for one or two days. Since these were highly publicized events, the propensity to "clean house" makes projecting an annual rate of disposal a very difficult task. Also, mean amount of waste per participant profiles were determined. The results indicated that men brought in about twice as much waste as women, and participants younger than 25 brought in the largest amount of waste per person. Although the latter group was only one percent of the participants, there was still a statistically significant pattern of more waste with decreasing age. Although the relationship is not very strong, college

Table 9

Summary of Minnesota Collection Project Wastes

Type	Ounces per Participant	Total Gals.	% of Total
Acid/Base	38.1	60.2	0.3
Adhesives	139.1	1082.2	6.2
Aerosol	5.3	72.7	0.4
Chlor. Solvents	32.0	81.6	0.4
Flam. Solvents	105.9	921.7	5.3
Latex Paint	291.1	3629.1	20.9
Nonhazardous	36.9	609	3.5
Oil	691.3	5986.4	34.4
Oil Paint	223.7	3882.1	22.3
Other	39.3	377.2	2.2
Pesticides	33.5	521.8	2.8
Rejected	91.7	137.8	0.3
Unknown	95.7	153.9	0.9

(Ridgley, 1987)

graduates had less wastes. Also, there was not a significant relationship between waste and dwelling ownership except in the area of home maintenance waste.

Finally, in an attempt to characterize the Household Hazardous Waste stream, a rather extensive list is being prepared by specific item and associated hazardous component (Tufts, 1987). Although the listing is very thorough with respect to the specific items that may be considered Household Hazardous Wastes, it is often not specific when identifying the hazardous component of a specific item, e.g., 'Heavy Metal.' However, this document is not yet in final form and, presumably, improvements will be made.

B. Leachate Generation Prediction

The moisture routing procedure for predicting leachate generation is based upon continuity (Remson et al, 1968). Continuity for any layer in a landfill indicates that the change in moisture storage for that layer is equal to moisture inflow minus moisture outflow. This method consists of moisture routing first through the cover soil of a landfill and subsequently through the underlying refuse. The cover soil and refuse are divided into layers for computational purposes. The available moisture to be routed through the cover soil is:

$$M_A = P - E/T - R/O \qquad (2.1)$$

where

M_A = Available moisture

P = Precipitation

E/T = Evapotranspiration

R/O = Runoff.

This available moisture is then either absorbed into the cover soil (+) or evaporated from the cover soil (-). The moisture in the cover soil will percolate into the landfill mass when the field capacity of the soil has been exceeded. In order to determine the net moisture addition to the cover soil to bring about this percolation, the following calculation is made:

$$W = (FC - IMC) \times D \times SA \qquad (2.2)$$

where

W = Water applied to cover soil (in)

SA = Unit surface area

FC = Field capacity of the soil (volume basis)

IMC = Initial moisture content (volume basis)

D = Depth of cover soil.

Water applied in excess of this amount will percolate into the underlying refuse. Leachate will then be produced when sufficient moisture has been percolated into the landfill

mass so that the field capacity of the solid waste is exceeded. Equation 2.2 is again used for this calculation, with all variables in terms of the landfill instead of the cover soil.

This method requires that the field capacity of the cover soil and the landfill mass be experimentally determined. Additionally, the model treats the landfill mass as biologically inert. Thus, the contribution of the moisture produced as a result of refuse decomposition is ignored. Also, the biodegradation may change the moisture storage characteristics of the landfill.

An empirical model for predicting leachate generation has been developed (Gee, 1985). Motivated by the fact that water balance methods give more reliable results in the long term, the author seeks to obtain accurate estimates of daily leachate generation. The basic assumptions of this model are that the sole source of infiltration is precipitation, i.e., groundwater does not enter the landfill, adjacent surface runoff is diverted, and there is no leachate recycle; and that the landfill mass is always at field capacity. By testing five different cover soils from operating landfills and field solid waste lysimeters - one sand, two silty sands, and two clays - the model was developed to predict leachate generation for a rainfall episode through any type soil:

$$Perc=e^{(K + \beta_1 \ln R + \beta_2 \ln(\omega_i/\omega_f) + \beta_3 \ln\gamma_d + \beta_4 \ln a + \beta_5 C_c)} \quad (2.3)$$

where

Perc = Percolation (in)

R = Daily rainfall (in)

ω_i = Initial moisture content (% dry weight)

ω_f = Field capacity (% dry weight)

γ_d = Dry density (pcf)

a = Slope (%)

C_c = Coefficient of curvature$=(D_{30})^2/(D_{60})(D_{10})$.

The coefficients were obtained from regression of the data for the five different soil types:

$K = 0.916$

$\beta_1 = 1.1683$

$\beta_2 = 6.5426$

$\beta_3 = -0.1567$

$\beta_4 = 0.08906$

$\beta_5 = -0.26881$.

The model accuracy was determined by comparison to field data and water balance methods. The model gave the best monthly and annual predictions, except in one case. However, there is no discussion of the model accuracy with respect to predicting daily leachate generation.

Additionally, the model accuracy depends heavily on the proper determination of the soil parameters.

C. Metal Ion Interactions

The concentration of free metal ions in landfill leachate results from the equilibrium between the different possible species of a particular metal. The interactions of metal ions, i.e., complex formation, adsorption, ion exchange, and hydrolysis/precipitation, all interrelate to determine the species of a metal present in the landfill and, therefore, the concentration of free metal ions in the leachate. A summary of these interactions is available in the literature (Jensen and Jorgensen, 1984).

There are many ligands available in landfill leachate, to include sulfate and acetate ions, which may form coordination complexes with the various metal ions. In addition to the competition between the various ligands to complex a metal ion, this complexation process also competes with the other previously mentioned metal ion interactions. Generally, complexation reactions mobilize metal ions, although these complexes may also be attenuated via adsorption, ion exchange, and precipitation.

Adsorption of metal ions on the surface of a solid substance results from surface forces that may include electrostatic attraction and hydrogen bonding (Parks, 1967). If chemical bonds are formed, the process is chemisorption. The law of mass action dictates that the

adsorption of metal ions will decrease as pH decreases, since the increasing number of hydrogen ions will occupy a larger number of adsorption sites. The determination of adsorption from multicomponent systems is detailed elsewhere in this literature review.

Ion exchange describes the process in which ions in solution replace ions of similar charge on the surface of a medium, also following the law of mass action. Ion exchange in multicomponent systems is complicated by the factors that govern the affinity of cations toward the exchanger (Scheffer and Schachtschabel, 1966) :

(1) Affinity increases with increasing valence number

(2) Affinity increases with a decrease in the diameter of the hydrated ion

(3) Species with higher charge densities have a greater affinity

(4) The geometry of the exchange surface

(5) Complexed ions are preferred to uncomplexed ions (Jenne, 1976).

Hydrolysis may solubilize metal ions, as in the case of aluminum trihydroxide, or it may cause the precipitation of an ion, as in the case of the formation of iron(III) trihydroxide (Stumm and Morgan, 1970). The solubility of metal ions increases with decreasing pH (Jorgensen and Johnsen, 1981). Also, hydrolysis of metal ions interferes

with the formation of coordination complexes (Friis et al, 1979). Finally, metal ions may be precipitated as a result of redox reactions, exemplified by the precipitation of iron in the form of FeS as it is reduced from Fe(III) to Fe(II) under anaerobic conditions.

The task is to determine which interactions are significant for which ions. Furthermore, understanding how these interactions interrelate under the conditions in the landfill and its associated leachate is essential in determining how metal ions are attenuated and to what extent.

D. Biodegradation of Organics

The biodegradation of many organic pollutants is well documented (e.g., Gibson, 1984, Hill and Wright, 1978, Charkrabarty, 1982). The specific microbes are identified, the metabolic pathways described, and the factors influencing biodegradation discussed. However, the specific kinetics and associated kinetic parameters are not well documented for the overwhelming majority of compounds. Furthermore, there is no indication in the literature of any studies on the biodegradation of pollutants in the landfill environment.

Presumably, the kinetics of the biodegradation of organic pollutants within a landfill are similar to those of other treatment process, e.g. wastewater treatment. In that case, the rate equation for an inhibitory substrate

(Yang and Humphrey, 1975) may be employed:

$$\frac{dS}{dt} = -\frac{\mu}{Y} = -\frac{\mu_m S}{Y\left(K_s + S + \frac{S^2}{K_i}\right)} \qquad (2.4)$$

where

μ = Specific growth rate

μ_m = Maximum specific growth rate

S = Substrate concentration

K_s = Saturation constant

K_i = Inhibition constant

Y = Yield coefficient

For the noninhibitory case (Monod, 1949):

$$\mu = \frac{\mu_m S}{K_s + S} \qquad (2.5)$$

may be used to describe the kinetics.

Alternatively, the kinetics of biodegradation may be described as a first-order reaction in which a threshold concentration must be attained before degradation will occur (Hill and Wright, 1978):

$$\frac{dS}{dt} = -k(S - S_0) \qquad (2.6)$$

where

k = First-order rate constant

S_0 = Threshold concentration.

No information is available for the kinetic parameters used in either model to estimate the biodegradation of organics in a landfill.

E. Adsorption from Multisolute Systems

Using statistical mechanics, the coefficients for an adsorption virial equation have been derived (Radke and Prausnitz, 1972). The number of solute molecules adsorbed is given by a power series expansion in the liquid phase concentration. For example, the total adsorption for a binary system as a function of the total concentration is:

$$N_1^a = B_1^+ c_1 + C_{11}^+ c_1^2 + C_{12}^+ c_1 c_2 + \cdots \qquad (2.7)$$

$$N_2^a = B_2^+ c_2 + C_{12}^+ c_1 c_2 + C_{22}^+ c_2^2 + \cdots \qquad (2.8)$$

where

N_i^a = Number of solute molecules adsorbed

B_i^+ = Adsorption second virial coefficient

C_{ij}^+ = Adsorption third virial coefficient

c_i = Solute concentration.

The adsorption second virial coefficient may be experimentally determined from the adsorption isotherm. This is accomplished by determining the slope of the

isotherm as the concentration of the solute approaches zero. Data from isotherms at several temperatures may then be regressed to determine the parameters Ad and ϵ^{*} in the statistical mechanical expression for B_i^{+}:

$$\frac{B_1^{+}}{Ad} = \frac{1}{10}\sum_{j=0}^{\infty} \frac{\left[5(20)^{2/3}\epsilon^{*}/12kT\right]^{(6j+1)/10}}{j!}\,\Gamma\left(\frac{4j-1}{10}\right) \quad , \quad (2.9)$$

where Γ is the gamma function. These parameters are then used to calculate the adsorption third virial coefficient, using the appropriate mixing rules for the cross coefficients ($i \neq j$).

The theoretical analysis presented is used to reduce experimental data for the adsorption on carbon of dilute aqueous isopropanol and aqueous propionitrile solutions. Although the extension of the adsorption virial equation to multisolute systems is straightforward, no experimental data are analyzed. Also, several areas in the application to multisolute systems may pose problems. Since a solution with X number of solutes has X^2 number of third virial coefficients, $X\sum_{n=1}^{X} n$ fourth virial coefficients, and so on, the virial equation must be truncated when evaluating for a large number of solutes in order to make the evaluation of N_i^{a} manageable. The point of truncation and the corresponding effect on accuracy must be determined.

Finally, gathering the experimental data will be a rather large task, as adsorption isotherms at several temperatures, the number based on the accuracy desired (upon regression) for the parameters, must be experimentally determined for each solute. However, once this is accomplished the temperature dependence of the adsorption virial coefficients will be known.

There exists a relationship, empirically determined, that allows the calculation of the mole fraction adsorbed of a particular solute in a multisolute system (Ościk, 1982). It was determined that when the ratio of mole fractions of the components of a binary solution i + k is, at equilibrium, equal to the ratio of the mole fractions of the same components in a multisolute system Σ_i,

$$\left(\frac{x_k}{x_i}\right)_{i,k} = \left(\frac{x_k}{x_i}\right)_{\Sigma_i} , \qquad (2.10)$$

then the ratios of the mole fractions adsorbed are also equal:

$$\left(\frac{x_k^a}{x_i^a}\right)_{i,k} = \left(\frac{x_k^a}{x_i^a}\right)_{\Sigma_i} . \qquad (2.11)$$

Therefore, it follows that:

$$(x_k{}^a)_{\Sigma_i} = \left[\sum_{i \neq k}^{n-1} (x_{i,k}^a)^{-1} - (n-2)\right]^{-1} , \qquad (2.12)$$

where n is the number of components in the system. Thus, the mole fraction adsorbed from the multisolute system is calcuated on the basis of that solute's adsorption isotherms from binary solutions with the the same mole fraction ratio as in the the multisolute system.

F. EP Toxicity Test

The EP Toxicity (EPTOX) Test is used to determine the concentrations of the hazardous components in a waste material. The waste material, in this case a municipal solid waste, is processed according to the procedure outlined below (National Bureau of Standards, 1986). The concentrations of the extracted contaminants are then compared to the regulatory levels for each item.

Procedure:

(1) A representative sample of waste (at least 100 grams) is collected.

(2) The liquid phase of the sample is removed and stored.

(3) If necessary, the solid phase of the sample is prepared for extraction by grinding so that it passes through a 9.5 mm sieve.

(4) The prepared solid phase is weighed and placed in an extractor vessel with 16 times its weight of deionized water.

(5) The extractor vessel is agitated for 24 hours at 20-40 ^{o}C. The pH of the solution is maintained at a maximum of 5.0 by the addition of .5N Acetic Acid.

(6) After 24 hours of agitation, deionized water is added to the extract in an amount determined by:

$$V = (20)(W) - (16)(W) - A \qquad (2.13)$$

where

V= Deionized water added to extractor (ml)

W= Dry weight of sample (grams)

A= .5N Acetic Acid added (ml).

(7) The extractor contents are now separated into liquid and solid phases.

(8) The liquids from steps 2 and 7 are combined and analyzed

The formula in step 6 will be used as a basis for developing the dilution model.

CHAPTER III

MODEL DEVELOPMENT

This model is developed in two phases. Initially, the model considers only the effects of dilution of the leachate on the concentration of a particular contaminant. First, the dilution by ground water is estimated based on the specific locale. Next, a method for determining the dilution by ground water is formulated based on the EPTOX Test. Finally, attenuation of leachate contaminants within the landfill mass is treated by the addition of an attenuation factor. However, the magnitude and "shape" of this parameter is, at present, unknown.

A. Dilution Model

This is a basic dilution model. Some operating assumptions are:

1. A contaminant is introduced into a landfill mass and is diluted by infiltrating water.

2. The landfill is treated as a plug-flow reactor with the flow parallel to the vertical axis and no radial concentration gradients.

3. The leachate generated by this infiltrating water may escape into the surrounding ground water; the quantity that escapes depends on the efficiency of the collection system.

4. The escaping leachate is diluted by ground water by an amount that is dependent on the specific locale.

The mass flow rate of the contaminant in the ground water, $\dot{M}_{gw}$, is:

$$\dot{M}_{gw} = Q_{gw} * C_{gw}, \tag{3.1}$$

where C_{gw}, the concentration of a contaminant in the ground water, is taken to be the drinking water standard for that particular contaminant. Q_{gw} is the ground water flow rate. But, this mass flow rate equals the mass flow rate of the contaminant in the leachate escaping from the landfill:

$$\dot{M}_{gw} = \dot{M}_{el}. \tag{3.2}$$

The concentration of the contaminant in the escaping leachate,

$$C_{el} = \dot{M}_{el} / Q_{el}, \tag{3.3}$$

equals the concentration in the leachate in the landfill:

$$C_{el} = C_{lf}. \tag{3.4}$$

The concentration of the contaminant in the leachate is:

$$C_{lf} = \dot{M}_{lf} / Q_{lf}. \tag{3.5}$$

Since the flow rate of the escaping leachate is equal to the difference between the flow rates of the leachate in the landfill and the leachate collected,

$$Q_{el} = Q_{lf} - Q_{coll}, \tag{3.6}$$

equations 3.1 - 3.6 may be written as:

$$\dot{M}_{lf} = \frac{Q_{lf}}{Q_{lf} - Q_{coll}} * Q_{gw} * C_{gw} \tag{3.7}$$

B. EPTOX-Based Dilution

If the dilution rate, λ, is defined as the ratio of the ground water flow rate to the flow rate of the escaping leachate,

$$\lambda = \frac{Q_{gw}}{Q_{el}}, \tag{3.8}$$

then equation 3.7 may be written as:

$$\dot{M}_{lf} = \lambda * Q_{lf} * C_{gw}. \tag{3.9}$$

In the EPTOX Test, the liquid phase removed initially is the analog of the initial moisture content of the landfill. Thus, the two subsequent additions of deionized water, the volume of which totals 20 times the weight of the sample, may be considered analogous to the leachate production by the landfill and the dilution of that leachate by ground water. Therefore, if the leachate flow rate from the landfill prior to interception by the collection system is known, then the ground water flow rate can be determined:

$$Q_{lf} + Q_{gw} = 20\ \rho V \tag{3.10}$$

where ρV is the mass of the landfill. However, to account for the effects of the somewhat rigorous extraction, this dilution rate of 20 times the mass of the sample should be spread over a longer period of time. This time factor, T, will now allow the the dilution factor to be calculated:

$$Q_{lf} + Q_{gw} = \frac{20\ \rho V}{T} \tag{3.11}$$

and

$$\lambda = \frac{Q_{gw}}{Q_{el}} = \frac{20 \rho V}{T\ Q_{el}} - \frac{Q_{lf}}{Q_{el}} \tag{3.12}$$

The mass of the landfill should be determined on the

same time scale as the leachate production. If Q_{lf} is in terms of volume/day, then the mass of the landfill would be the mass of the solid waste disposed in one day. This will account for the previous leaching of the underlying refuse. So, the equation for determining the mass flow rate of a contaminant into a landfill necessary to exceed the ground water standard for that particular contaminant is:

$$\dot{M}_{lf} = \left[\frac{20\rho V}{T\ Q_{el}} - \frac{Q_{lf}}{Q_{el}}\right] * C_{gw} * Q_{lf}\ . \qquad (3.13)$$

C. Attenuation Factor

A parameter, η, is added to the dilution model to account for the attenuation of contaminants. The effects of each of the attenuation processes may be separated out. For organics:

$$\eta = \eta_{ad} + \eta_{bd} \qquad (3.14)$$

or for metal ions:

$$\eta = \eta_{ad} + \eta_{ie} + \eta_{cf} + \eta_{hp} \qquad (3.15)$$

where

η_{ad} = attenuation due to adsorption

η_{bd} = attenuation due to biodegradation

η_{ie} = attenuation due to ion exchange

η_{cf} = attenuation due to complex formation

η_{hp} = attenuation due to hydrolysis/ precipitation.

The importance of each of the individual attenuation factors will depend on the individual contaminant. No attempt will be made to estimate the magnitude of the attenuation factor as the attenuation processes in a landfill environment are not well understood.

CHAPTER IV

DISCUSSION

The purpose of this discussion is to illustrate the use of the dilution model and examine the results in light of the aforementioned studies conducted to determine the character of Household Hazardous Wastes. Since metal ions and many of the solvents may have several sources, the following sample calculation is for a pesticide. Thus, the source of the contaminant is unambiguous.

A. Sample Calculation

The goal of this calculation is to determine the amount of the pesticide Diazinon that must be discarded into a sanitary landfill in order to exceed the drinking water standard of 0.7 μg/l (New York State Law). The data for the landfill are based on a muncipal landfill operated in upstate New York. This particular landfill services approximately 33,000 people. It receives an average of 22,000 tons of solid waste per year. The average daily leachate production is approximately 1000 gallons, of which 900 gallons are intercepted by the leachate collection system. Therefore,

$$C_{gw} = 0.7\ \mu g/l$$

$$Q_{tl} = 1000\ gpd$$

$$Q_{el} = 100\ gpd$$

The average daily mass of solid waste disposed of is:

22,000 tons x 2000 lbs/ton / 365 days = 13,076 lbs/day

The sum of the escaping leachate flow rate and the groundwater flow rate is (assuming that the time factor, T, is 1):

$$Q_{lf} + Q_{gw} = \frac{20\rho V}{T} = \frac{20*13,076}{1} * .12\ CF = 31,382 \text{ gallons}$$

and the dilution factor is:

$$\lambda = \left[\frac{20\rho V}{T\ Q_{el}}\right] - \frac{Q_{lf}}{Q_{el}} = \frac{31,382}{100} - 10 = 303.82$$

Therefore, the mass flow rate of Diazinon necessary to exceed the ground water standard of 0.7 μg/l is:

$$\dot{M}_{lf} = \lambda * C_{gw} * Q_{lf} = 303.82*0.7*1000*3.785x10^{-6}CF$$

$$= 0.805 \text{ g/day} = 0.027 \text{ fl oz/day}$$

B. Interpretation

Since Diazinon is normally sold as a 25% by weight liquid, the actual amount of "off the shelf" liquid, based on the amount calculated above, is 0.108 fl oz. This is, obviously, a very small amount. In comparison, the results of Rathje et al, will be applied to the operational

parameters of the sample calculation. The amount of the solid waste stream that is hazardous is:

13,076 lbs/day x 0.4% = 52.3 lbs/day

Using the two weight fractions of pesticides/lawn care found in Table 8, the expected range is:

52.3 lbs/day x 8.8% = 4.60 lbs/day

52.3 lbs/day x 1.0% = 0.52 lbs/day

or between approximately 8 and 71 fl oz of pesticides/lawn care items in the solid waste stream. Of course, all of this is not necessarily *Diazinon, however,* if it was, then the range would be 2 to 18 fl oz, using the 25% by weight figure. Since there is no further breakdown of the pesticide/lawn care category, it is difficult to determine the characteristics of this portion of the Household Hazardous Waste stream and, therefore, be able to estimate the fraction of this category that is Diazinon.

Even though the result for this sample calculation was obtained using real-life operational parameters, it is based on dilution only. Therefore, the result is the worst-case for the given dilution rate since no account is taken of the possible attenuation of the contaminant. Thus, the implication is that this model is unable to make

a general statement on the impact of Household Hazardous Wastes. It is, however, able to determine the impact of a specific contaminant on a given landfill and its associated operational parameters.

The dilution model gives the expected results in the obvious limits of the operational parameters. As the efficiency of the leachate collection system increases, or the leachate produced in the landfill decreases, each causing the escaping leachate flow rate to decrease, the dilution factor becomes very large. Since the mass flow rate of the contaminant into the landfill necessary to exceed the regulatory limit is directly proportional to the dilution factor, it also becomes increasingly large. This behavior confirms the landfill management strategies of infiltration reduction and leachate collection.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

The literature review and the dilution model serve to amplify the research necessary to determine the impact of Household Hazardous Wastes on landfill leachates. These research needs include:

1. The database on Household Hazardous Waste could be improved in several ways. Seasonal variations of this waste stream need to be documented. The categories of Household Hazardous Wastes should be characterized in more detail. It is necessary to know the particular components and associated weight fractions of, for example, the pesticide/lawn care category. Also, it would be beneficial to identify the particular form and amount of a contaminant in its associated Household Hazardous Waste.

Source	Form
Used Motor Oil	?
Stain	?
Varnish	?

The form of the contaminant will dictate its solubility in leachate, e.g., Lead (Weast, 1984):

Item	Solubility
$Pb(C_2H_3C_2)_2$	443 g/l (282 g Pb/l)
$Pb(C_2H_3O_2)_2*3H_2O$	456 g/l (249 g Pb/l)
$PbCl_2$	9.9 g/l (7.4 g Pb/l)

2. An understanding of the attenuation processes occuring in the landfill would enhance the results from the dilution model. As the minumum, an order of magnitude estimate of the attenuation of a contaminant would greatly improve the efficacy of the model. For metal ions, the significant interactions for each metal must be identified and the relationships among these interactions must be determined. Also, research is necessary to determine the kinetics of biodegradation of organics in the landfill. The proper kinetic model must be ascertained and the associated kinetic parameters determined. The adsorption of contaminants from leachate must be assessed, perhaps, by using the methods of Radke and Prausnitz or Ościk.

3. The estimation method for leachate dilution by ground water, based on the EPTOX Test is untested. The determination of this dilution will, in all likelihood, be necessary on a site-by-site basis. Although the numerical and analytical methods available for solving the ground water flow problem are generally not easy to use, they may be used to determine the accuracy of the EPTOX-based method.

4. Leachate generation must be accurately predicted in order to apply the dilution model. Therefore, easy-to-use methods, such as the direct method (Gee, 1985), must be verified to ensure that they can accurately predict leachate generation on both a short-range and long-range basis.

When a better understanding of these research areas is achieved, an accurate assessment of the impact of Household Hazardous Wastes will be possible. Then, perhaps, a determination can be made as to which components of this portion of the solid waste stream may be disposed of in a landfill and those which require an alternative means of disposal.

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